

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 September 2001 (13.09.2001)

PCT

(10) International Publication Number
WO 01/66650 A2

(51) International Patent Classification⁷: **C09B 67/04, 67/12**

10063 Fox Chase Drive, Loveland, OH 45140 (US).
SCHWARTZ, Russell, J.; 8300 Monte Drive, Cincinnati,
OH 45233 (US). **MAC CUNE, Karii, L.**; Apartment 4,
6637 Gracely Drive, Cincinnati, OH 45233 (US).

(21) International Application Number: PCT/US01/07367

(22) International Filing Date: 7 March 2001 (07.03.2001)

(74) Agent: **PERSLEY, Sidney**; 222 Bridge Plaza South, Fort
Lee, NJ 07024 (US).

(25) Filing Language:

English

(81) Designated State (national): CA.

(26) Publication Language:

English

(84) Designated States (regional): European patent (AT, BE,
CH; CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,
NL, PT, SE, TR).

(30) Priority Data:

09/520,482

8 March 2000 (08.03.2000) US

Published:

— without international search report and to be republished
upon receipt of that report

(71) Applicant: **SUN CHEMICAL CORPORATION**
[US/US]; 222 Bridge Plaza South, Fort Lee, NJ 07024
(US).

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(72) Inventors: **WILLIS, Michael**; 7138 Virginia Av-
enue, Cincinnati, OH 45236 (US). **MERCHAK, Paul**;



WO 01/66650 A2

(54) Title: PROCESS FOR PRODUCING β -PHASE COPPER PHTHALOCYANINE PIGMENT

(57) Abstract: A process for the preparation of β phase copper phthalocyanine pigment which includes dry grinding crude copper phthalocyanine in the absence of a grinding aid to obtain a crude mill; and conditioning the crude mill in about 5 to 50 wt.% based on the weight of the crude mill of a conditioning solvent.

PROCESS FOR PRODUCING β - PHASE
COPPER PHTHALOCYANINE PIGMENT

5

FIELD OF THE INVENTION

This invention relates to a process for converting crude copper phthalocyanine into β - phase copper phthalocyanine pigment.

10

BACKGROUND OF THE INVENTION

Crude copper phthalocyanine (CuPc) pigment is non- or partially-substituted and when obtained directly from solvent or non-solvent synthetic routes is generally in a coarse crude form that is non-pigmentary, tinctorially weak, and requires further processing. By "crude" we mean a pigment obtained in a highly aggregated form having a particle size not suitable for use as a pigment, or pigment which has been milled to produce a product which is also aggregated and has a broader particle size distribution than that obtained from synthesis but is still unsuitable for use as a pigment or an industrial colorant for inks and/or coatings. This processing involves comminution (e.g. milling) to reduce the particle size, and/or further conditioning to obtain pigmentary quality. Several conventional primary comminution processes include, for example, dissolving or swelling crude pigment in different concentrations of sulfuric acid, precipitating it in water, and kneading it in combination with milling aids (i.e., inorganic salts) and solvents. Wet milling or dry milling are typically carried out for example in a ball mill with or without milling aids. When the primary route of comminution is by dry grinding, typical a conditioning process follows

- 2 -

and may include: slurring or suspending the milled-crude in an aqueous, aqueous-organic or organic solvent and heating and/or wet-milling, or mixing in a dense mass state with water-soluble solvent and inorganic salt to provide pigmentary quality material.

Pigment processing by wet and dry milling of crude organic pigments is described in the prior art. They often require conditioning the wet or dry milled crude pigment in a slurry, at an elevated temperature, with large amounts of water, solvent, surfactants and/or combinations of these along with other additives. The fluids used are typically used in the range of up to 100 wt.% or more of the milled crude.

It is desirable, however, to minimize the amount of water, organic salts, solvent and additives used during pigment synthesis process since most of these compounds or solvents must be removed in order to isolate the CuPc pigment. This can be time-consuming and thus expensive. Furthermore, using less organic solvents is preferred because of environmental considerations. Lower process temperatures are also preferred as this helps to minimize crystallite growth and this is important since larger pigment crystals lose color strength and are more opaque.

SUMMARY OF THE INVENTION

The present invention relates to a dry process for producing β -phase CuPc pigment and with excellent color value. Specifically, the β -phase CuPc pigment is prepared by grinding crude CuPc in the absence of

grinding aids then dry conditioning in a conditioning solvent that is present in low amounts.

DETAILED DESCRIPTION OF THE INVENTION

5 It has now been found that pigmentary grade β -phase CuPc can be produced by dry grinding crude CuPc in the absence of grinding aids to obtain a crude mill and subsequently conditioning the crude mill in the presence of a low amount of conditioning solvent.

10 The first process step of the present invention involves dry milling, in an industrial grinding mill such as a ball mill, attritor, or vibratory mill, the crude. No grinding aids (i.e. inorganic salts) are present
15 during milling. The milling conditions, which include the grinding media size, shape and composition, milling time and temperature, are mill dependent. The aggregated product (e.g. crude mill) will be an $\alpha:\beta$ mix mostly of the β -phase and have, as determined by X-Ray diffraction, i.e.
20 from 0:100 to 80:20. More preferably the target $\alpha:\beta$ ratio is from 50:50 to 65:35 when no milling solvents are present and from 0:100 to 65:35 when milling solvents are used. The crude mill will have a surface area, of less
25 than 10 m²/gm and consists of primary particles of less than 0.10 microns in size. The dry milling step may also be performed in the presence of low amounts of milling solvent and other additives.

 Milling solvents may be used in amounts less than 50% preferably 10% of the weight of the crude CuPc,
30 and at combinations of these along with other additives. The fluids typically are employed in amounts ranging up to 100% by weight or more of the crude mill.

- 4 -

The second process step of the present invention involves conditioning the crude mill, for example, in an industrial mixer to a free-flowing granular powder form with a conditioning solvent and optionally a dispersant or other additive to form. The dry magma which is formed shall contain about 25 to 95 wt.%, preferably about 45 to 65 wt.% of the crude mill; conditioning solvent weighing about 5 to 50 wt.%, preferably about 20 to 40 wt.% of the crude mill; dispersant being about 0 to 20 wt.%, preferably about 5 to 15 wt.% of the crude mill; and additives (such as resins or waxes) being about 0 to 50 wt.% of the crude mill. The crude mill is then conditioned and/or recrystallized by mixing under shearing for 1 to 15 hours, preferably for 2 to 8 hours, at a temperature of less than about 120°C, more preferably between about 80 to 110°C, and most preferably between about 90 to 100°C in an industrial mixer.

Industrial mixers include but are not limited to a sigma or disperser blade mixer, a double planetary mixer, a vacuum drier with or without rotating chopper blades, a conventional dough mixer, a mix muller, an extruder or any mixing or grinding unit that is capable of applying a mechanical shear or mixing.

Milling and conditioning solvents are used here to describe organic materials that are non-solid at the conditioning temperature and pressure. The conditioning solvent may be of a recrystallizing type or a non-crystallizing type, with the recrystallizing type preferred when the crude mill contains α -form CuPc that

- 5 -

needs to be recrystallized to β -form CuPc. When all β -form CuPc crude mill is obtained either type of solvents may be used. Incorporated into the scope of this invention is that any combination of the two types, or
5 two or more of either types may be used, though a single solvent is preferred.

Preferably, the conditioning solvent is selected from the group consisting of glycols, fatty
10 acids, plasticizers (such as dioctyl phthalate and epoxidized soya oil), amphoteric surfactants (such as nonylphenolethoxylates), hydrocarbon petroleum distillates and alkylene carbonates. More preferably, the conditioning solvent is a glycol such as a glycol
15 selected from the group consisting of diethylene glycol, dipropylene glycol, polyethylene glycol, monoethylene glycol monoether, triethylene glycol monoether and glycol ether esters (such as butyl carbitol acetate).

Pigment dispersing agents and other
20 conventional additives may be added before, during or after the dry grinding, conditioning or isolation processing steps. They help improve wetting, dispersibility, dispersion stability and coloristic
25 properties (strength, gloss, transparency, etc.) of the CuPc pigment.

Examples of dispersants include but are not limited to $\text{CuPc}-(\text{X})_n$, wherein n is an integer from 1 to 6;
30 X is selected from the group consisting of SO_3M^+ , SO_2R , and CH_2Y ; M is selected from the group consisting of hydrogen, primary, secondary, tertiary, or quaternary

- 6 -

amine; R is selected from the group consisting of metal ion, dimethyl amino propylamine, phthalimide, and amine terminated polyalkylene oxide; and Y is selected from the group consisting of NH_2 , phthalimide, and o-carboxy benzamide.

Examples of conditioning additives include but are not limited to various types of rosins, polymeric resins, waxes, plasticizers, crystal growth inhibitors and extenders.

The resulting CuPC pigment product can be further processed or incorporated directly into, for example, an ink formulation to provide excellent color value.

An optional third process step can be employed in the present invention when it is desirable to isolate the pigmentary CuPC product. It involves isolation of the pigment by removing the milling or conditioning solvents and can be performed by distillation, filtration or by other methods known to those ordinary skill in the field of solvent removal. The presscake obtained from using a conventional filter press typically employed at the end of a solvent removal step may be dried and ground by conventional methods known in the field. However, solvent removal may be avoided altogether if the milling and conditioning solvent, dispersant and additives have specifically chosen to remain in the product as having compatibility with the final application of the product as a colorant.

- 7 -

Example 1

Conventional crude CuPc (12 lbs.) is dry milled for 24 hours in a ball mill containing 100 lbs. of 2 inch diameter steel balls at 70°C. The aggregated mill crude was analyzed and determined to be composed of a 60:40 α : β mix of CuPc, composed of primary particles averaging 0.04 microns in size.

The crude mill (12 lbs.) was then transferred to a Mix Muller (mixer) in which diethylene glycol (3.6 lbs.) was added while mixing. Steam was applied to the heating jacket of the mixer to keep the temperature during the mixing cycle at 100°C. After a 2 hour mixing cycle at 100°C, CuPc-SO₂-primary amine (0.7 lbs.) was added. The resulting product was mixed for 3 hours at about 100°C then added to water (5 parts) and the pH was adjusted with hydrochloride to 1.5. The resulting slurry was stirred for 2 hours at 85°C, filtered and washed with water to a pH of about 7. The resulting presscake was dried and determined to have excellent color value in a nitrocellulose packaging ink systems.

Example 2

Conventional crude CuPc (12 lbs.) was dry milled for 24 hours in ball mill, containing 100 lbs. of 2 inch diameter steel balls at 70°C. The aggregated crude mill was determined to be composed of a 60:40 α : β mix of CuPc composed of primary particles averaging from 0.02 to

- 8 -

0.04 microns in size.

The crude mill (12 lbs.) was then transferred to a Mix Muller in which hydrocarbon petroleum distillate (3.6 MagieSol® 47) was added while mixing. Steam was applied to the heating jacket of the mixer for 5 hours to keep the temperature at about 100°C. The resulting magma was dispersed in an offset oil ink systems and offered excellent color strength.

10

Example 3

Crude CuPc was dry milled in a ball mill for 8 hours. This material was then transferred to a stainless steel kneader (800 mil capacity) in which diethylene glycol (105 grams) was added while mixing. Steam was applied to the kneader to heat the jacket to keep the temperature at 100°C. The resulting magma was added to water (2 liters) and the pH was adjusted with hydrochloride to 1.5. The slurry was stirred for 2 hours at 85°C, filtered and washed with water to a pH of about 7. The resulting presscake was used as an aqueous dispersions and was reported to have excellent color strength value.

25

The invention has been described in terms of preferred embodiments thereof, but is more broadly applicable as will be understood by those skilled in the art. The scope of the invention is only limited by the following claims.

30

What is claimed is:

1. A process for preparing β copper phthalocyanine pigment comprising:

5 (a) dry grinding crude copper phthalocyanine in the absence of a grinding aid to obtain a crude mill; and

(b) conditioning the resulting crude mill in a conditioning solvent present in an amount ranging from about 5 to 50 wt.% based on the weight of the crude mill
10 at a temperature sufficient for producing pigment.

2. The process of Claim 1 wherein the β copper phthalocyanine pigment is separated from the conditioning solvent and optional dispersant or other
15 conditioning additives.

3. The process of Claim 1 wherein the amount of the conditioning solvent is about 20 to 40 wt.%

20 4. The process of Claim 3 wherein the conditioning solvent is selected from the group consisting of glycols, fatty acids, plasticizers, amphoteric surfactants, hydrocarbon petroleum distillates, and alkylene carbonates.

25 5. The process of Claim 4 wherein the conditioning solvent is a glycol.

30 6. The process of Claim 5 wherein the glycol is selected from the group consisting of diethylene glycol, dipropylene glycol, polyethylene glycol, monoethylene glycol monoether, triethylene glycol

- 10 -

monoether and glycol ether esters.

7. The process of Claim 1 wherein the conditioning is carried out at a temperature less than
5 120°C.

8. The process of claim 7 wherein the conditioning is carried out between about 80 and about
10 110°C.

9. The process of Claim 1 further comprising adding a dispersant or conditioning additive during the conditioning step.

15 10. The process of Claim 9 wherein the dispersant is $\text{CuPc}-(\text{X})_n$, wherein n is an integer from 1 to 6; X is selected from the group consisting of SO_3M^+ , SO_2R , and CH_2Y , M is selected from the group consisting of hydrogen, primary, secondary, tertiary, or quaternary
20 amine; R is selected from the group consisting of metal ion, dimethyl amino propylamine, phthalimide, and amine terminated polyalkylene oxide; and Y is selected from the group consisting of NH_2 , phthalimide, and o-carboxy benzamide.

25 11. The process of Claim 9 wherein the conditioning additive is selected from the group consisting of rosins, polymeric resins, waxes, plasticizers, crystal growth inhibitors, and extenders.

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
13 September 2001 (13.09.2001)

PCT

(10) International Publication Number
WO 01/66650 A3

(51) International Patent Classification⁷: C09B 67/04.
67/12, 67/50

SCHWARTZ, Russell, J.: 8300 Monte Drive, Cincinnati, OH 45233 (US). MAC CUNE, Karii, L.: Apartment 4, 6637 Gracely Drive, Cincinnati, OH 45233 (US).

(21) International Application Number: PCT/US01/07367

(74) Agent: PERSLEY, Sidney: 222 Bridge Plaza South, Fort Lee, NJ 07024 (US).

(22) International Filing Date: 7 March 2001 (07.03.2001)

(25) Filing Language: English

(81) Designated State (national): CA.

(26) Publication Language: English

(84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

(30) Priority Data:
09/520,482 8 March 2000 (08.03.2000) US

Published:
— with international search report

(71) Applicant: SUN CHEMICAL CORPORATION
[US/US]; 222 Bridge Plaza South, Fort Lee, NJ 07024 (US).

(88) Date of publication of the international search report:
14 March 2002

(72) Inventors: WILLIS, Michael: 7138 Virginia Avenue, Cincinnati, OH 45236 (US). MERCHAK, Paul: 10063 Fox Chase Drive, Loveland, OH 45140 (US).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 01/66650 A3

(54) Title: PROCESS FOR PRODUCING β -PHASE COPPER PHTHALOCYANINE PIGMENT

(57) Abstract: A process for the preparation of β phase copper phthalocyanine pigment which includes dry grinding crude copper phthalocyanine in the absence of a grinding aid to obtain a crude mill; and conditioning the crude mill in about 5 to 50 wt.% based on the weight of the crude mill of a conditioning solvent.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/07367

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09B67/04 C09B67/12 C09B67/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 221 466 A (BASF CORP) 13 May 1987 (1987-05-13) abstract; examples ---	1-11
Y	US 4 024 154 A (JACKSON JULIUS) 17 May 1977 (1977-05-17) abstract column 3, line 53 -column 4, line 13 ---	1-11
Y	US 4 141 904 A (CABUT LOUIS A ET AL) 27 February 1979 (1979-02-27) abstract; examples 6-8 ---	1-11
Y	CH 478 213 A (GEIGY AG J R) 15 September 1969 (1969-09-15) column 2, line 3 - line 19 column 3, line 7 - line 65; examples 8,11,12 --- -/-	1-11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *8* document member of the same patent family

Date of the actual completion of the international search

31 August 2001

Date of mailing of the international search report

19/09/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Dauksch, H

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/07367

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category "	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 199605 Derwent Publications Ltd., London, GB; Class E23, AN 1996-045488 XP002176477 & JP 07 310024 A (DAINIPPON INK & CHEM INC), 28 November 1995 (1995-11-28) abstract</p> <p style="text-align: center;">---</p>	1-11
A	<p>US 3 849 150 A (POLSTER R ET AL) 19 November 1974 (1974-11-19) abstract; examples 2-4,10,11</p> <p style="text-align: center;">---</p>	1-11
A	<p>EP 0 407 831 A (BASF AG) 16 January 1991 (1991-01-16) the whole document</p> <p style="text-align: center;">-----</p>	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/07367

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0221466	A	13-05-1987	US 4709021 A CA 1285710 A JP 62112660 A	24-11-1987 09-07-1991 23-05-1987
US 4024154	A	17-05-1977	NONE	
US 4141904	A	27-02-1979	FR 2265826 A BE 827085 A BR 7501736 A CH 621569 A DE 2512610 A DK 100075 A GB 1495625 A IT 1030426 B JP 50157419 A NL 7502906 A	24-10-1975 24-09-1975 23-12-1975 13-02-1981 02-10-1975 26-09-1975 21-12-1977 30-03-1979 19-12-1975 29-09-1975
CH 478213	A	15-09-1969	GB 1140836 A DE 1619568 A DK 118908 B FR 1512124 A JP 51001732 B US 3523030 A	22-01-1969 30-07-1970 19-10-1970 18-04-1968 20-01-1976 04-08-1970
JP 7310024	A	28-11-1995	NONE	
US 3849150	A	19-11-1974	DE 2132546 A AT 325732 B AT 560072 A AU 459937 B AU 4352272 A BE 785654 A CH 565229 A DK 144797 B FR 2143945 A GB 1402011 A IT 965862 B JP 55006670 B NL 7208768 A SE 389510 B	18-01-1973 10-11-1975 15-01-1975 26-03-1975 20-12-1973 02-01-1973 15-08-1975 07-06-1982 09-02-1973 06-08-1975 11-02-1974 19-02-1980 03-01-1973 08-11-1976
EP 0407831	A	16-01-1991	DE 3922734 A DE 59005160 D DK 407831 T ES 2062200 T JP 3045659 A US 5175282 A	24-01-1991 05-05-1994 02-05-1994 16-12-1994 27-02-1991 29-12-1992

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.